214-1B6(First Quarter)

FIRST QUARTERLY REPORT

STUDY OF THE GROWTH PARAMETERS INVOLVED IN SYNTHESIZING BORON CARBIDE FILAMENTS

by

A. Gatti, E. Feingold, V. A. Cordua

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GPO PRICE $ ____

CFSTI PRICE(S) $ ____

Hard copy (HC) 2.00

Microfiche (MF) .50

ff 653 July 65

May 20, 1966

CONTRACT NASw-1383

Space Sciences Laboratory
GENERAL ELECTRIC COMPANY
Missile and Space Division

FACILITY FORM 602

N66 28480 (ACCESSION NUMBER)

(THRU)

29 (PAGES)

1 (CODE)

CR-75715 (NASA CR OR TMX OR AD NUMBER)

18 (CATEGORY)

TABLE OF CONTENTS

LIST OF FIGURES

STUDY OF THE GROWTH PARAMETERS INVOLVED IN SYNTHESIZING BORON CARBIDE FILAMENTS

by

A. Gatti, E. Feingold, V. A. Cordua
General Electric Company

SUMMARY

The purpose of the present program has been the investigation of the following:

1. The growth of B_4C whiskers.
2. Characterization of the B_4C whiskers in terms of mechanical properties and crystalline perfection.
3. Incorporation of B_4C whiskers in composite specimens.

B_4C whiskers have been grown in a chimney type graphite resistance furnace which uses the temperature gradient developed at the chimney top to control the supersaturation of B_4C vapor for subsequent nucleation and growth of the whiskers. The geometry of the whisker growth zone of this furnace causes the whiskers to grow curved instead of the more desirable straight variety.

A second furnace was developed to provide a more uniform thermal gradient in the growth region. The results obtained by using this second furnace were encouraging, and straight whiskers were produced. However, the current yield in the newer furnace is composed of very short whiskers, which are probably too short to effectively reinforce metal matrices.

Studies were continued on investigating the effects of the growth and deposition-zone geometry of the chimney type furnace on whisker production. A new geometry was used which has increased the yield of B_4C whiskers per run by a factor of ten.

Curved B_4C whiskers were annealed for 5 hours at 1900°C. The curvature, which occurred during the standard whisker runs, appears to have been annealed out following this treatment. The annealed whiskers also appear to have smoother surfaces. Room temperature tensile tests on

annealed specimens were made to determine if an upgrading of the strength properties of the whiskers was achieved. It so far appears that the annealing treatment has had only a weakening effect.

It had been observed that curved whiskers were susceptible to breakage even when handled very carefully. X-ray studies of these curved whiskers were made to determine the magnitude of residual stresses which could occur because of the curvature. The studies indicated that compressive residual stresses of the order of 100,000 PSI are present in the as-grown curved B_4C whiskers. This sizable stress can explain the apparent weakness of such whiskers.

I. INTRODUCTION

Boron Carbide (B_4C) whiskers exhibit attractive properties for utilization in composite materials. In terms of their high strength, low density and high elastic modulus, these whiskers when utilized as reinforements, offer a great potential for high strength-to-weight or high stiffness-to-weight materials for future space applications. In addition, their refractory properties make them valuable also for high temperature applications.

Although more than one method of B_4C whisker growth has been studied, the most successful one to date has been the pure vapor method[1]. This method consists of the vaporization of B_4C powder at high temperatures and subsequent condensation of B_4C whiskers on a graphite substrate at a lower temperature. It has been used to study the growth parameters and to obtain an adequate whisker supply for composite fabrication.

Further geometric changes in the whisker deposition area has led to increased whisker production and to reduction of the number of curved whiskers.

It has been observed that long time annealing of B_4C whiskers at high temperatures resulted in the straightening of curved whiskers. Tensile tests on annealed specimens have been initiated but thus far annealing has not up-graded the strength of B_4C whiskers.

Characterization of B_4C whiskers is necessary to establish the nature of the whisker product. These studies of physical structure offer another method of product quality assessment.

X-ray studies of a curved whisker have shown that internal stresses on the order of E/600 (ca. $\sim$100,000 psi) are possible, further emphasizing that curvature must be minimized in whiskers which are to be used in composites.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. GROWTH STUDIES

Previous work had shown that a radial type furnace[2] produced large quantities of straight B_4C whiskers. However, the whiskers were very short with the longest specimen approaching 0.2 inches in length.

It has been shown by Kelly[3] and others[4] that a critical length of reinforcing fiber is necessary before a transfer of stress from a matrix of a reinforcing fiber can occur. A rather simple relationship is derived by which an estimation of this critical length can be made, viz.:

$$L_c = \frac{\bar{\sigma}_f \, d_f}{2\tau} \qquad (1)$$

Where L_c = critical length for reinforcement

$\bar{\sigma}_f$ = strength of fiber

d_f = fiber diameter

τ = shear strength of matrix (or interface)

Assuming that the law of mixtures is valid, L_c then approximates the minimum length of whisker necessary to initiate any reinforcement. Another deriviation also attributable to Kelly[3] is:

$$\sigma_c = V_f \, \bar{\sigma}_f \left(1 - \frac{\ell_{cf}}{2\ell_f}\right) + \text{(matrix contribution)} \qquad (2)$$

ignoring any matrix contribution to composite strengthening.

Where

σ_c = strength of the composite

V_f = volume fraction of the fibers in a composite

ℓ_f = length of the fibers.

By combining equations (1) and (2) it is apparent that to use 95% of the available strength of any fiber, the fiber length must be at least 10 times ℓ_c. Also from equation (1) as τ decreases, with temperature (as would be expected) then ℓ_f would necessarily have to be even greater than $10\,\ell_c$ for a 95% utilization of $\overline{\sigma}_f$.

Assuming an average diameter of 10 microns for B_4C whiskers, an average strength per whisker of 500,000 psi and a τ of 3,000 psi for aluminum at room temperature, $\ell_c \simeq .010$ inches. Thus whiskers which are shorter than 0.1 inch should be undesirable.

Studies to increase the lengths of the radial furnace type whisker have proved unsuccessful. Thus it has been necessary to rely completely upon the chimney type furnace for a whisker supply of sufficient length to be useful for composite studies. Therefore, studies to both foster increases in the number of whiskers grown per run in the chimney furnace and means for minimizing curvature of the as grown whiskers were initiated.

1. Chimney Geometry Studies

The results of earlier studies showed that the geometric configuration of the whisker deposition area of the chimney type furnace influenced the size and number of whiskers grown. The evolution of the internal mandrel design[5] was a direct result of this discovery. Another modification of the deposition zone has led to further enhancement of growth. The internal mandrel has been replaced by the thin, crossed, flat plates shown in Figure 1. The deposition area has thus been increased by approximately 20 times. An increase of approximately an order of magnitude in the number of whiskers grown per run has been noted.

An added result of the geometric change has been the reduction of the number of curved whiskers grown. This occurs presumably because of the alteration of the symmetrically shaped temperature gradients which were present in the former deposition geometry.

B. WHISKER ANNEALING STUDIES

Many of the B_4C whiskers grown by the vapor method used here are

66-DI-174

Figure 1. Photograph (About 1/2 Size) of Modified Internal Mandrel Design

curved and also have growth steps on their surfaces. Curved B_4C whiskers have recently been studied by X-ray techniques and the results are presented later in this report (see Section IIIA). The B_4C whiskers which contain severe growth steps can be weakened significantly because these growth steps could act as stress raisers with notch efficiences of 5 to 10.

Previous results[2] had shown that such areas undergo a change in geometry after extensive annealing. Therefore, experiments were performed during this report period to determine whether annealing improves the properties of B_4C whiskers.

A graphite annealing box was designed which held an internal growth mandrel in an upright position. Figure 2 is a schematic assembly drawing of the annealing box. The box containing an internal mandrel was placed into the chimney furnace such that it was heated uniformly to 1900°C in vacuum and was held at temperature for 5 hours. Examination of the whiskers after annealing showed that significant changes had indeed occurred. Whiskers were notably less curved, and appeared smoother. Figure 3A is a typical internal mandrel scraping before annealing which shows a proponderance of curved whiskers. Figure 3B is a scraping of annealed whiskers which contains no curved whiskers at all. Figure 4 is a photomicrograph which shows the smooth surface of a typical annealed whisker. Comparison of this surface with previously examined as grown surfaces[5] show a definite trend toward smoother surfaces.

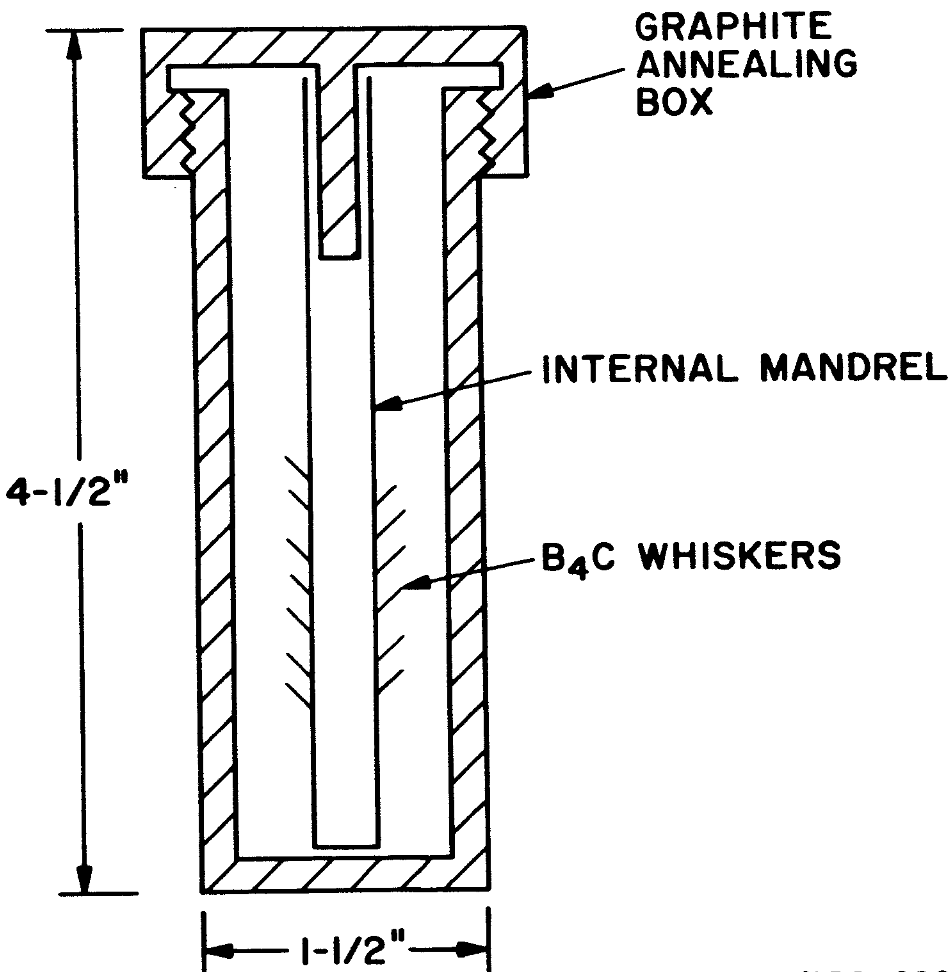
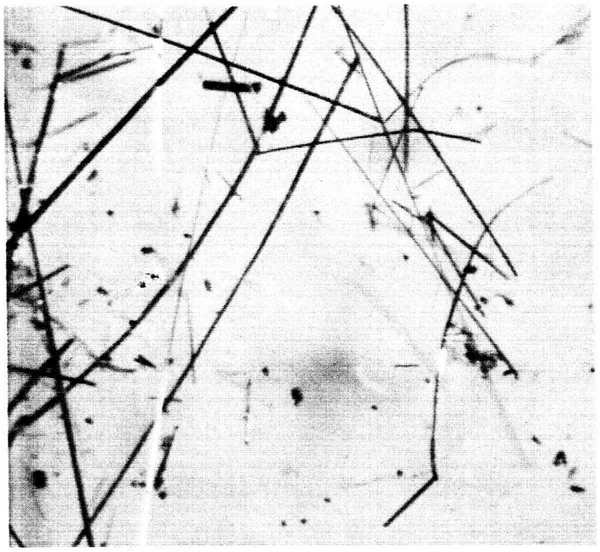
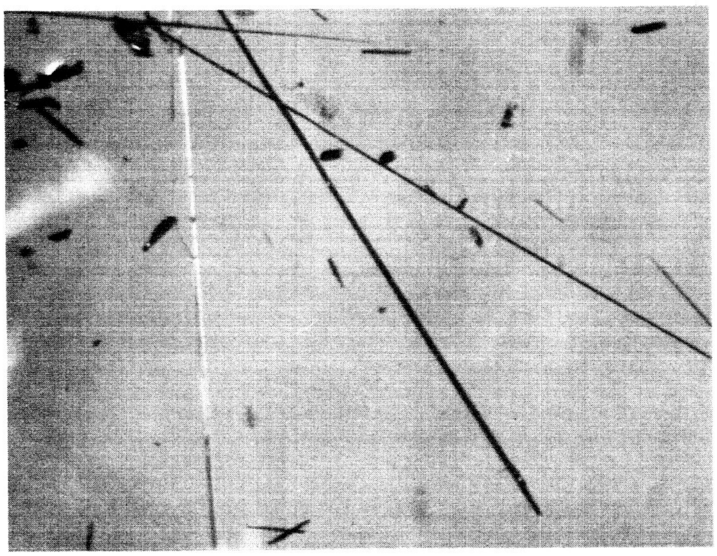


Figure 2. Schematic Assembly Drawing of Graphite B_4C Whisker Annealing Box.



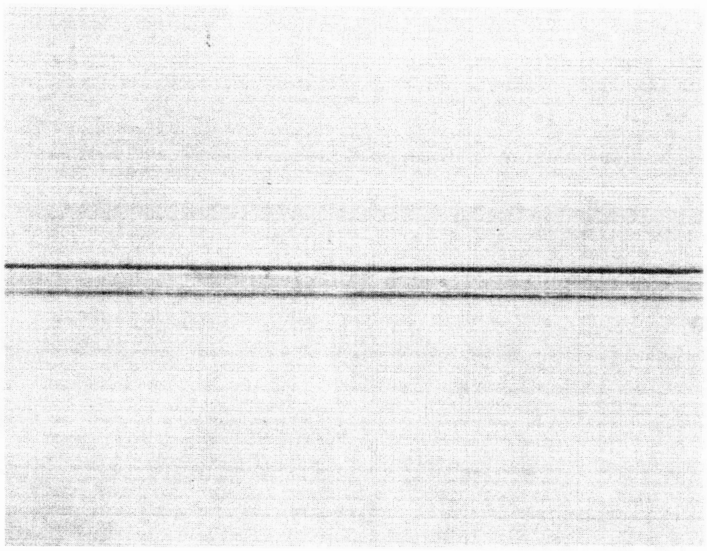
A



B

66-DI-173

Figure 3. Eamples of Curved B_4C Whiskers as They Appear
A) Before Annealing - 30X.
B) After Annealing - 30 X.



66-DI-175

Figure 4. Example of Whisker Surface of An Annealed Whisker - 300X.

III. WHISKER CHARACTERIZATION

A. X-RAY DIFFRACTION

It had been observed that severely curved B_4C whiskers could not survive even slight manipulation during handling. They would tend to shatter in the region of high curvature. Therefore, it appeared that this type of whisker probably contained internal residual stresses.

During this report period an x-ray diffraction analysis was begun in order to elucidate the internal stress character of curved B_4C whiskers. It was planned that precision lattice parameters a_o and c_o (hexagonal unit cell edges) would be obtained from the curved and straight portions of individual whiskers. If indeed there existed internal stresses one could detect this fact by observing differences in the magnitude of lattice parameters when comparing the curved with the straight portions of the same whisker. In this way the magnitude and type (compression or tension) of stresses could be determined. Analysis was completed only on a single curved B_4C whisker before equipment failure occurred. The results of this analysis will now be described.

1. Discussion and Results

Hexagonal unit cell parameters (a_o and c_o) were determined from interplanar separation measurements ($d_{(hh0)}$ and $d_{(00\ell)}$ respectively). A General Electric single crystal orienter mounted on a G.E. XRD-5 diffractometer and nickel filtered copper radiation was used. The chosen curved B_4C whisker was mounted (using a very small drop of Duco Cement) on the end of a 1/10 mm diameter glass filament. After careful alignment, d_{110}, d_{220}, d_{330} and d_{003}, d_{006}, d_{009}, $d_{00.12}$, $d_{00.15}$ were determined for both the curved and straight portions of the whisker. The lattice parameters were then calculated from the hexagonal unit cell relationship:

$$\frac{1}{d^2_{(hk\ell)}} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{\ell^2}{c^2} \qquad (3)$$

For the two types of interplanar spacings, namely $d_{(hh0)}$ and $d_{(00\ell)}$ the above relation can be written

$$a = 2h\, d_{(hh0)} \tag{4}$$

$$c = \ell\, d_{(00\ell)} \tag{5}$$

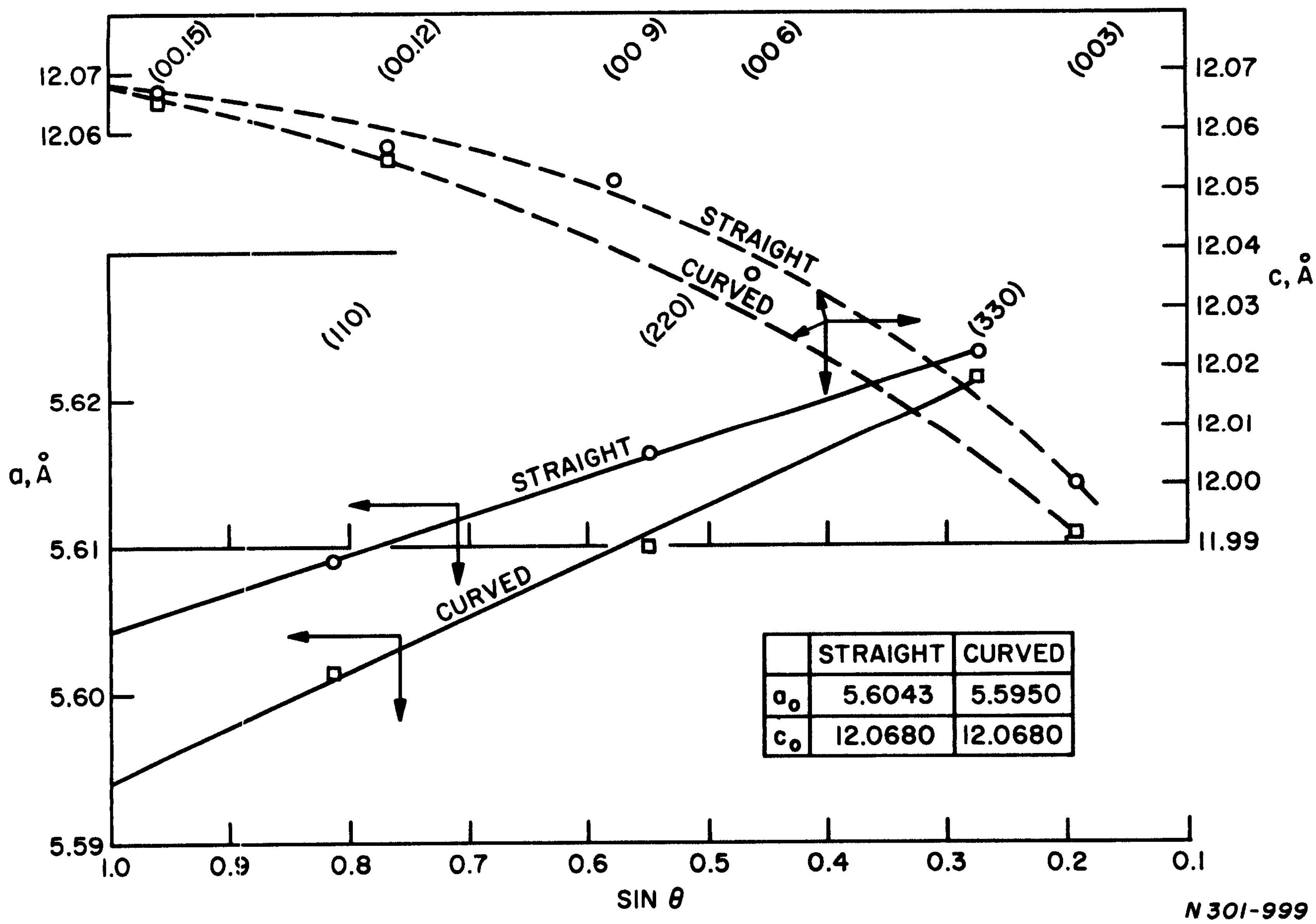
The experimentally determined d-spacings and the corresponding a and c values are presented in Table I.

TABLE I

Experimental Interplanar Spacings, d, and Calculated Lattice Parameters a and c

	Straight		Curved	
hkl	d(Å)	a(Å)	d(Å)	a(Å)
110	2.8115	5.6230	2.8098	5.6196
220	1.4041	5.6164	1.4025	5.6100
330	0.93464	5.6078	0.93361	5.6017
	d(Å)	c(Å)	d(Å)	c(Å)
003	4.0012	12.0036	3.9973	11.9919
006	2.0060	12.0360	----	----
009	1.3391	12.0519	----	----
00.12	1.0048	12.0576	1.0046	12.0552
00.15	0.80448	12.0672	0.80437	12.0655

A graphical extrapolation of the above data to $\theta = 90$ degrees was then performed and a_o and c_o values were obtained. The extrapolation was done using sine θ, see Figure 5. In Figure 6 is a sketch of the whisker used in this investigation. The curved major axis of this whisker, like all of its straight counterparts was found to be everywhere parallel to the $\vec{a}$ cyrstallographic direction. Shown in this Figure are: A and B, the curved and straight portions respectively from which x-ray diffraction data were obtained; and the orientation of the whisker with respect to the hexagonal unit cell directions. From the data presented in Figure 5 it may be seen that the interatomic separations in the c-direction (i.e., $\langle 00\ell \rangle$) are the



	STRAIGHT	CURVED
a_o	5.6043	5.5950
c_o	12.0680	12.0680

Figure 5. Hexagonal Unit Cell Lattice Parameters a_o and c_o for Curved and Straight Portions of a Single B_4C Whisker.

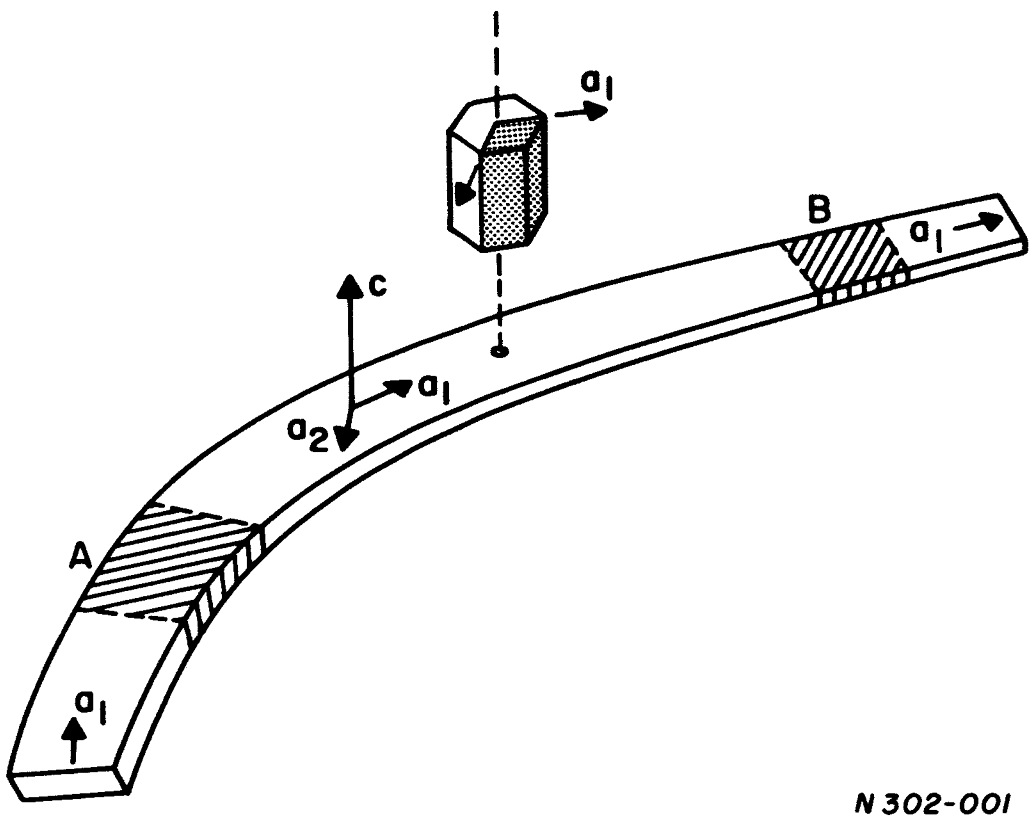


Figure 6. Sketch of Curved B_4C Whisker. Lattice Parameters (a and c) were Determined from Curved Section A and Straight Portion B (a_o^A = 5.5950Å, c_o^A = 12.0680Å, a_o^B = 5.6043Å, c_o^B = 12.0680Å).

same for both the straight and curved portions of the whisker. However, the interplanar separation in the a-direction shows a contraction in the curved portion.

The contraction of $\vec{a}$ corresponds to a compressive strain in the curved portion of the whisker. Assuming that the straight portion of the whisker is unstrained* then one is able to calculate the strain in the direction of curvature to be:

$$\epsilon^{(curved)} = \frac{a_o^{(straight)} - a_o^{(curved)}}{a_o^{(straight)}}$$

$$\epsilon^{(curved)} = \frac{5.6043 - 5.5950}{5.6043}$$

$$\epsilon^{(curved)} = 0.00166 \approx \frac{1}{600}$$

Thus, the internal stress σ^i in the curved portion of the whisker is (where E = modulus):

$$\sigma^i = E\,\epsilon^{(curved)}$$

$$= \frac{E}{600}$$

Considering that the strongest whiskers (B_4C) tested to date have strengths in the order of 2×10^6 psi or $\frac{E}{30}$, the internal compressive stress is sizeable and this explains the observed weak character of severely curved whiskers. In Figure 7 is shown a spring analog of an internally stressed, curved B_4C whisker. The curved portion A is shown under compression

---

* This assumption is not thought to be unreasonable since the lattice parameters obtained from the straight portion are in good agreement with ASTM values. Lattice parameters: straight portion (a_o = 5.6043Å, c_o = 12.068Å), ASTM values (a_o = 5.61Å, c_o = 12.07Å).

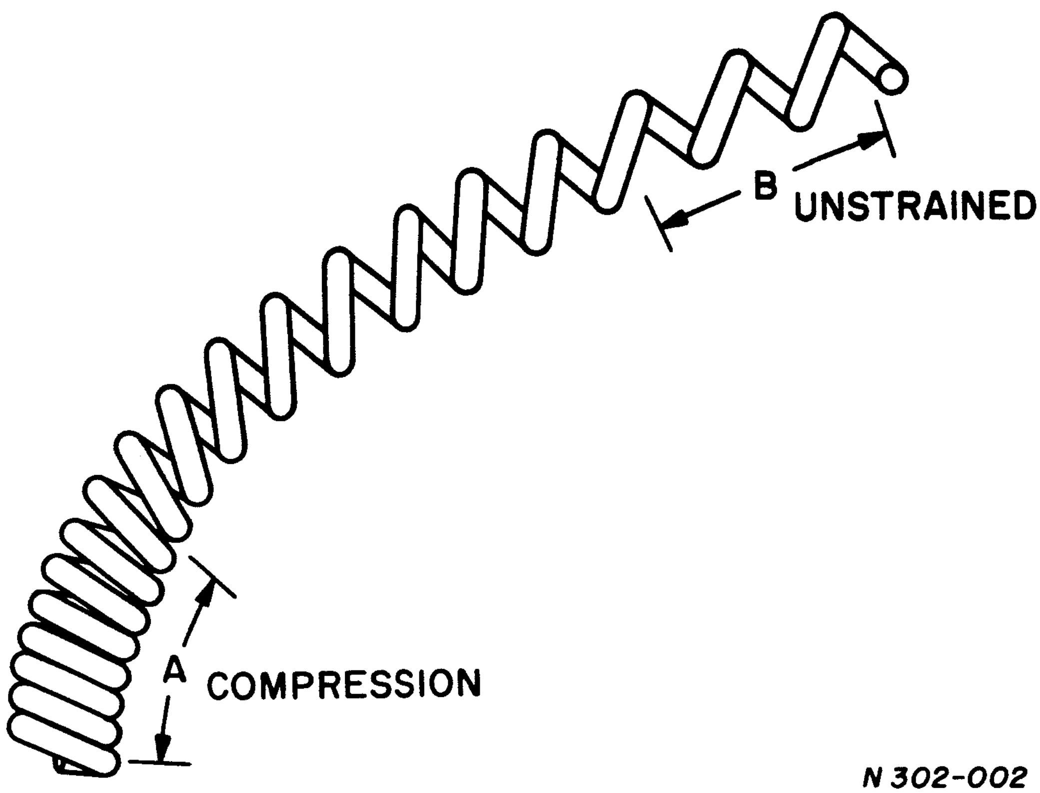


Figure 7. Spring Analog of Internal Stresses in Curved B_4C Whisker.

while the region B is unstrained. This, of course, is not an equilibrium condition, which readily explains catastrophic failure when a slight amount of energy is added to the system as, for example, when an attempt is made to handle or manipulate these curved whiskers.

Additional analysis of curved B_4C whiskers will be made in the future.

B. MECHANICAL PROPERTIES

Annealed B_4C whiskers are noticably more smooth and straighter than as-grown whiskers. Such changes in surface character and internal structure could lead to an up-grading in the strength characteristics of B_4C whiskers. Accordingly, samples of long, smooth straight annealed whiskers were tested in tension. The technique used for these tests have been previously described.(5)

The tensile data on 6 samples tested thus far are presented in Table II. A large reduction in average strength over the previous tensile data is apparent. Thus, although the annealed whiskers appear more perfect (ca. stronger) the present tensile data does not confirm this assumption. Of course, no attempt at optomization of the annealing treatment has yet been made. Also, detailed studies of the annealed whisker surfaces have just begun so that the tentative conclusions of surface improvement made earlier must be examined under more discriminating conditions including electron microscopy.

TABLE II

Strength of Annealed and As Grown B_4C Whiskers

SPEC NO.	LT (mm)	LO (mm)	AREA (μ^2)	σ m (PSI)
HEAT TREATED				
1	1.50	0.60	92.6	100,000
2	1.84	0.55	43.5	336,000
3	2.90	0.77	43.6	147,000
4	4.24	0.57	71.5	169,000
NOT HEAT TREATED				
1	---	0.87	141.3	873,000
2	4.51	0.35	22.4	760,000

IV. CONCLUSIONS

1. Further work on the radial type furnace has been curtailed because of the apparent limit on the length of B_4C whiskers which can be grown by this equipment. Whiskers produced using the radial furnace are not 5 to 10 times longer than the calculated critical length thought necessary for reinforcement. Efforts to overcome this length deficiency have proved unsuccessful.

2. A change in the deposition geometry of the standard chimney type furnace has led to an increase in whisker number/growth run to approximately 10 times that which was obtained previously. It is felt that this result is an important contribution because it is the second time during the development of B_4C whisker technology that an order of magnitude increase in growth has been achieved. The geometry change has also apparently altered the temperature gradient structure of the deposition area so that more long, straight whiskers are being grown.

3. X-ray diffraction studies of curved whiskers have shown that residual stresses of the order of 100,000 psi are present. Such residual stresses are certainly not desirable and means must be found to avoid growing curved whiskers or minimizing the effects by annealing, etc.

4. A study of the effects which annealing whiskers has on their curvature and structure was initiated. Curvature is removed from all whiskers examined and their surfaces appear smoother when they are annealed for 5 hours at 1900°C in vacuum. Thus far, the strengths of annealed whiskers have been disappointing. Further studies will be made to elucidate these effects.

V. FUTURE WORK

1. Growth studies utilizing a revised deposition geometry will continue.

2. Whisker annealing studies will be extended in an attempt to optimize temperature, time and atmosphere parameters so that long, straight, smooth strong whiskers will result.

3. Detailed surface studies of annealed whiskers will be made to ascertain the degree of surface change resulting from annealing.

4. A supply of long straight whiskers are being accumulated for another attempt at forming strong aluminum-B_4C whisker composites by an infiltration method. Composites using these selected whiskers will be made during the next report period.

References

1. A. Gatti, et al, "Synthesis of Boron Carbide Filaments", NASw-670, Final Report, July 10, 1964.

2. A. Gatti, et al., "Study of the Growth Parameters Involved in Synthesizing Boron Carbide Whiskers", NASw-1205, Final Report, March 1, 1966.

3. A. Kelly and G. J. Davies, "The Principles of Fibre Reinforcement of Metals", Met. Rev., 1965, Vol. 10, No. 37.

4. W. H. Sutton and J. Chorné, "Potential of Oxide-Fiber Reinforced Metals", Fiber Composite Materials, ASM 1964.

5. A. Gatti, et al, "Study of the Growth Parameters Involved in Synthesizing Boron Carbide Filaments", NASA CR-251, July 1965.

Acknowledgements

Acknowledgement is given to Mr. T. Harris for his valuable assistance in the program.